

Ferroelectricity induced by cooperative orbital ordering and Peierls instability.

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A general mechanism by which orbital ordering, coupled to Peierls-like lattice distortions, can induce an electronic switchable polarization is discussed within a model Hamiltonian approach in the context of the modern theory of polarization. By using a Berry-phase approach, a clear picture emerges in terms of Wannier-function centers and orbital occupancies. The proposed mechanism may apply to oxide spinels whose electronic structure has effective one-dimensional character, such as CdV_2O_4 , recently proposed to display multiferroic behaviour.

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Introduction. Since the revival of interest in the magnetoelectric effect and in the multiferroic state of condensed matter[1–3], the possible electronic, as opposed to purely ionic, origin of ferroelectric polarization has attracted, and still attracts, increasing attention[4, 5]. A significant contribution to the field came from the rigorous definition of macroscopic bulk polarization \mathbf{P} in crystal lattices, as given in the early 90's, which eventually led to the formulation of what is nowadays known as the modern theory of polarization[6–8]. According to this theory, polarization changes can be formally expressed in terms of the Berry phase (BP) of the electronic wavefunctions, which correctly captures the contribution to \mathbf{P} coming from mobile electrons in crystals with covalent character - what is generally referred to as the electronic contribution to polarization. Several mechanisms responsible for electronic ferroelectricity has been devised since, involving spin[9, 10], charge[11, 12] and orbital[13, 14] degrees of freedom of electrons.

Due to its potential straight application in magnetoelectric devices, the first class of mechanisms, that applies directly to magnetically induced ferroelectrics, has been object of intense research[2, 9, 10]. Nonetheless, our understanding of general mechanisms leading to electronically induced ferroelectricity cannot neglect the implications of charge- (CO) or orbital-ordering (OO) phenomena. The essential mechanism by which a charge ordering can lead to a bulk polarization is fairly well understood [3, 12]. Ferroelectricity, in fact, may arise due to a simultaneous inequivalency of both sites and bonds after charge ordering, a situation often found in transition metal compounds containing transition metal ions with different valence. Bond inequivalency may be structural, as for example in quasi one-dimensional organic materials (such as $(\text{TMTTF})_2\text{X}$ [15] or TTF-CA [16]), or may have a magnetic origin, as in the case of $\text{Ca}_3\text{CoMnO}_6$ [17] or RNiO_3 [18], where ferromagnetic and antiferromagnetic bonds differentiate through symmetric exchange striction. The simultaneous presence of site-centered and bond-centered CO has been also proposed to induce ferroelectricity in half-doped manganites

such as $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ or $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [11]. In this case, however, we have suggested that orbital degrees of freedom may play a relevant role in establishing the ferroelectric state[19]. The interplay of electron-electron ($e-e$) and electron-lattice ($e-l$) interaction, in particular the coupling with the buckling mode associated to rotation of the oxygen cages ubiquitous in perovskite oxides, causes an effective dimerization via an orbital striction mechanism, also responsible for the predicted OO pattern[20, 21]. Quite surprisingly, OO combined with the forementioned effective dimerization appears to be the main source of an electronically induced polarization, since CO is strongly inhibited in the dimerized state[19].

In our opinion, these findings call for further research and suggest that the role of OO in establishing or contributing to ferroelectric polarization deserves a deeper understanding. In order to provide a clear picture of the possible general mechanisms by which \mathbf{P} can be induced by OO, therefore, we analyze within the BP approach a simple one-dimensional tight-binding model where OO can be controlled by a Hubbard-like interaction. We will consider only spinless fermions, which allow to easily disentangle the role of spin and charge from orbital degrees of freedom in causing a finite polarization. We will show that bond inequivalency without CO but with a finite orbital-occupancy disproportionation is enough to lead to a ferroelectric state, provided the intra-orbital hopping interactions are different. The choice of this extremely simple model is motivated by the clear insight it provides within the BP framework, rather than by its straight application to some real material. Nonetheless, we expect the proposed mechanism to be rather general and possibly relevant for the recently proposed multiferroic vanadium spinel CdV_2O_4 [22] and similar systems, as we discuss in our concluding remarks.

Model and analytical formulas. The possible interplay between orbital degrees of freedom and bond inequivalency in inducing a bulk \mathbf{P} can be addressed by considering a spinless two-band Peierls-Hubbard model, defined

on a one-dimensional chain, whose Hamiltonian reads:

$$H = \sum_{j,\gamma,\gamma'} t_j^{\gamma\gamma'} (d_{j\gamma}^\dagger d_{j+1\gamma'} + h.c.) + \frac{K}{2} \sum_j u_j^2 + U \sum_j d_{j1}^\dagger d_{j1} d_{j2}^\dagger d_{j2}, \quad (1)$$

with $d_{j\gamma}^\dagger$ creating an electron in the orbital γ of site j . The hopping parameters are modulated by the $e-l$ interaction, with coupling constant α , as $t_j^{\gamma\gamma'} = t^{\gamma\gamma'} [1 + \alpha(u_j - u_{j+1})]$, where u_j are the displacement of the ions from their equilibrium position along the chain, with the associated elastic constant K . Without loss of generality, in the following we will neglect any inter-orbital hopping, assuming $t_j^{\gamma\gamma'} = \delta_{\gamma,\gamma'} t_\gamma$ with $t_1 \neq t_2$. The last term describes the Coulomb interaction between electrons occupying different orbitals, parametrized by the Hubbard constant U .

Let us consider the half-filling case with average local occupation fixed to $n = 1$ [23]. Peierls-like dimerization can be realized via a staggered pattern of distortions $u_j = (-1)^j u_0$, with u_0 to be variationally determined, whereas the Coulomb interaction can be decoupled via standard Hartree-Fock linearization. The model is then formally equivalent to a single-band spinful Peierls-Hubbard model, whose staggered magnetization $m = (-1)^j (n_{j\uparrow} - n_{j\downarrow})$ maps to the difference between average orbital occupancies $\Delta = (-1)^j (n_{j1} - n_{j2})$, that may serve as the order parameter for orbital ordering. Since the periodicity of dimerization and of staggered OO is the same, the Hamiltonian in reciprocal space can be defined in the reduced Brillouin zone, reading

$$h_k^\gamma = \begin{pmatrix} \varepsilon_\gamma(k) + \frac{1}{2}U & \delta_\gamma(k) + (-1)^\gamma \frac{1}{2}U\Delta \\ \delta_\gamma^*(k) + (-1)^\gamma \frac{1}{2}U\Delta & -\varepsilon_\gamma(k) + \frac{1}{2}U \end{pmatrix} \quad (2)$$

in each orbital sector, where $\varepsilon_\gamma(k) = -2t_\gamma \cos k$ and $\delta_\gamma(k) = i4\alpha u_0 t_\gamma \sin k$, with both u_0, Δ to be self-consistently determined. Eigenstates are given by:

$$E_\pm^\gamma(k) = \frac{1}{2}U \pm \sqrt{\varepsilon_\gamma(k)^2 + |\delta_\gamma(k)|^2 + \frac{1}{4}(U\Delta)^2}, \quad (3)$$

implying an insulating groundstate for nonvanishing u_0 or Δ , which at half filling must fulfill the following self-consistency equations:

$$\frac{4\pi}{U} = \sum_{\gamma,k} \left[\varepsilon_\gamma(k)^2 + |\delta_\gamma(k)|^2 + \frac{1}{4}(U\Delta)^2 \right]^{-1/2}, \quad (4)$$

$$\frac{\pi K}{8\alpha^2} = \sum_{\gamma,k} \frac{t_\gamma^2 \sin^2 k}{\sqrt{\varepsilon_\gamma(k)^2 + |\delta_\gamma(k)|^2 + \frac{1}{4}(U\Delta)^2}}. \quad (5)$$

Depending on the coupling constants α, U , four phases are found characterized by different structural and orbital properties. For small α and $U = 0$, we found a metallic

ground-state, with no orbital-occupancy disproportionation and no structural distortion. As U, α are increased, three different insulating ground-states develop with finite Δ or u_0 . A first insulating phase, with $\Delta \neq 0$ and $u_0 = 0$, is induced by increasing the $e-e$ interaction, exactly mapping onto the antiferromagnetic insulator found for the half-filled single-band Hubbard model. On the other hand, a dimerized state, with $u_0 \neq 0$ and $\Delta = 0$, develops with increasing α at small U , which is the conventional Peierls insulator with structural distortions. A third insulating phase intrudes between the first two at moderate values of U by increasing the $e-l$ interaction; this insulating state is characterized by the coexistence of OO and structural dimerization. The phase diagram in the $U-\alpha$ space is shown in Fig. 1 for a given ratio between hopping parameters, namely $t_1/t_2 = 3$. The evolution of dimerization u_0 and orbital occupancy disproportionation Δ is also shown as a function of U , highlighting the coexistence regions at different values of the $e-l$ interaction. Even if the phase boundaries depend on the ratio t_1/t_2 and may be affected by the mean-field approximation, the phase diagram is qualitative the same as the one obtained for the single-band Peierls-Hubbard model by more accurate numerical methods[24].

Turning to ferroelectricity, the key quantity to be considered is the overlap matrix defined as $S_{m,m'}(k, k') = \langle \psi_{m,k} | e^{-i\frac{2\pi}{L}\hat{x}} | \psi_{m',k'} \rangle$, which allows to evaluate the expectation value of the position operator \hat{x} on the eigenstates $\psi_{m,k}$, with m the occupied band index, which obey periodic boundary conditions on a 1d chain of length L [25]. Since the overlap matrix has nonvanishing elements only when each pairs of k, k' differs by $\epsilon = 2\pi/L$,

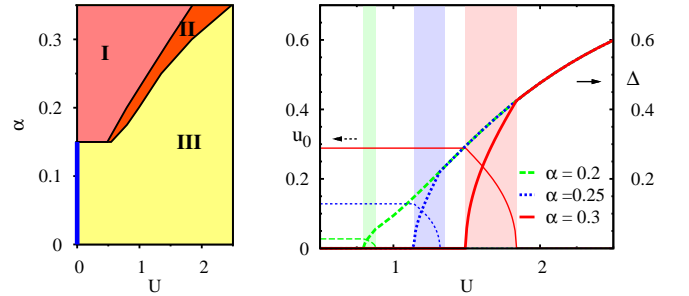


FIG. 1: Left: Phase diagram in the $U-\alpha$ space for the two-band spinless Peierls-Hubbard with inequivalent hoppings $t_1/t_2 = 3$: the thick line represents the metallic solution found at $U = 0$, I and III label respectively the Peierls and OO insulator, with II the mixed-character insulator intruding between them. All parameters are expressed in units of $t = (t_1 + t_2)/2 = 1$ and the elastic energy is fixed to $K = 1$. Right: evolution of the dimerization parameter u_0 (thin lines) and of the orbital-occupancy disproportionation Δ (thick lines) as a function of U for different values of the $e-l$ interaction. Regions where OO coexists with structural distortion are highlighted.

one can explicitly evaluate its elements on the eigenstates of Hamiltonian (2) in the limit of $L \rightarrow \infty$, finding $S_{m,m'}(k, k + \epsilon) = \delta_{m,m'}(1 + i\epsilon S_m)$ with:

$$S_m = (-1)^m \frac{4\epsilon_m(k)^2}{E_+^m - E_-^m} \frac{\alpha u_0 U \Delta}{(U\Delta)^2 + 4|\delta_m(k)|^2} \quad (6)$$

where $m = 1, 2$ labels the occupied bands with eigenvalues $E_+^1(k), E_-^2(k)$ as given in Eq. (3). By assuming an uniformly charged ionic background, no ionic contribution arises from the chain distortion in the absence of charge disproportionation; polarization, then, has only an electronic origin and is evaluated as[25]:

$$\frac{\pi}{e}P = -\text{Im} \sum_k \log \det S(k, k + \epsilon) \simeq - \int_{-\pi/2}^{\pi/2} \sum_m S_m dk, \quad (7)$$

e being the electron charge. By inspecting Eqs. (6),(7) it comes clear that two conditions must be simultaneously fulfilled in order to have a nonvanishing P : i) both OO and structural dimerization, with $u_0\Delta \neq 0$, must occur, and ii) hopping integrals must be different in different orbital channels, i.e. $t_1 \neq t_2$, otherwise the two addends in the r.h.s of Eq. (7) would cancel out exactly leading to $P = 0$. The explicit expression for $S_m(k)$, as given in Eq. (6), also implies that the polarization can be reversed either by swapping the orbital occupancy between the two inequivalent sites in the doubled cell or by interchanging short and long bonds of the distorted chain. A paradigmatic evolution of P in the dimerized orbital-ordered state is shown in Fig. (2). Enforcing the correspondence between the two-band spinless and one-band spinful Peierls-Hubbard model, one immediately recognizes that the second condition is never fulfilled in the spinful model, since hopping integrals are spin independent and identical. This explains why the antiferromagnetic ground state of the single-band Peierls-Hubbard model is never ferroelectric unless a CO is realized, e.g., by including a staggered potential, as already discussed in Ref. 16.

A pictorial interpretation of the origin of the electronic P in the orbital-ordered dimerized state is provided by looking at the center of the Wannier functions (WF) of the two occupied bands, that are easily evaluated for the 1d system under consideration. As pointed out in Ref. 26, in fact, the construction of maximally localized WFs is not needed in the present case; WF centers can be obtained as the eigenvalues of a matrix Λ , constructed as the product of the unitary parts of the S matrices along the k-point string (given by the matrix product VW^\dagger taken from the singular value decomposition $S = V\Sigma W^\dagger$, where V and W are unitary and Σ is a diagonal matrix with nonnegative diagonal elements). In the limit of infinite chain (with $\epsilon \rightarrow 0$), it turns out that the WF centers r_m are given by the two addends in the r.h.s of Eq. (7), a

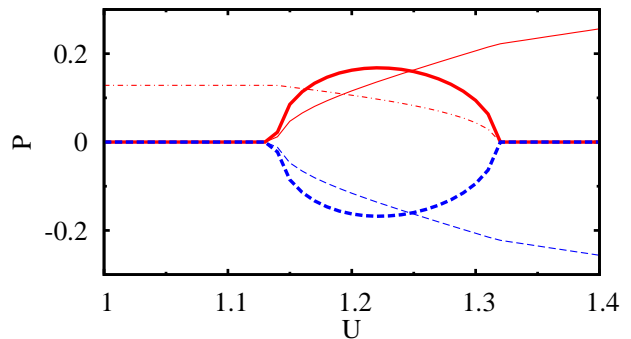


FIG. 2: Evolution of the Berry-phase polarization (thick lines) as a function of U at $\alpha = 0.25$ and $t_1/t_2 = 3$. Thin lines are the dimerization parameter u_0 (dot-dashed line) and the OO parameter Δ (solid or dashed); dashed lines correspond to the swapping of orbital occupancy by keeping fixed the structural distortion of the chain, causing a reversal of P .

well-known result in the context of the modern theory of polarization[8]. That means that in the orbital-ordered dimerized state the two WF centers move in opposite directions along the chain, reflecting the staggered orbital occupancy; the different hopping integrals $t_1 \neq t_2$ (implying $|S_1| \neq |S_2|$), however, make the displacements of r_m with respect to their nonpolar positions inequivalent, giving rise to uncompensated local dipoles that sum up resulting in a bulk P . This is shown in Fig. 3, where the evolution of r_m is plotted as a function of U for $\alpha = 0.25$ and $t_1/t_2 = 3$. In the Peierls insulator, where bonds differentiate in alternating short and long ones, both the WF centers lie in the middle of the short bond. On the other hand, when OO develops, e.g. with prevalent $\gamma = 1$ character on odd sites and $\gamma = 2$ on even sites, the corresponding WF centers move towards the most occupied sites with same orbital character. Due to the different values of hopping integrals, these displacements are inequivalent and cause the local dipoles to be uncompensated. Eventually, when the structural distortion disappears in the OO insulator, each r_m lies on a site of the chain, as schematically shown in Fig. 3b).

Conclusions. We analysed the ferroelectric properties of a simplified model in the framework of the modern theory of polarization in order to unveil the necessary conditions by which OO phenomena may lead to an electronic bmP . The spinless two-band Peierls-Hubbard model allowed us to consider the cooperative interplay between OO and Peierls-like dimerization along a 1d chain. The derived analytical formulas, even if obtained at a mean-field level, clarify that P may arise from OO only if a concomitant bond inequivalency (appearing as a structural dimerization in the considered model) develops. Naïvely, the emerging P may be interpreted as a superposition of two inequivalent charge-localization phenomena in different orbital sectors. By looking at Wannier-function

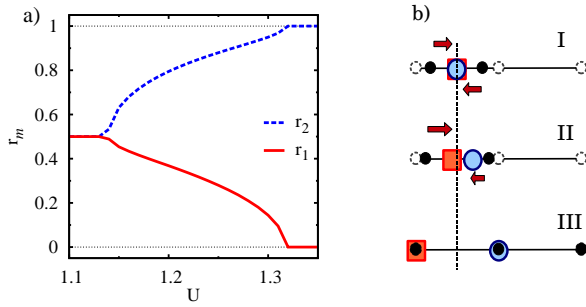


FIG. 3: *a)* Evolution of the Wannier function centers r_m , in units of lattice spacing $a_0 = 1$, as a function of U for $\alpha = 0.25$ and $t_1/t_2 = 3$. *b)* Schematic picture of the displacement of WF centers as the system evolves from the Peierls insulator (I) to the OO insulator (III) through the dimerized orbital-ordered state (II), highlighting the inequivalent local dipoles that develops in phase II (empty circles indicate the undistorted position of sites along the chain; the displacements are exaggerated to make the picture clearer).

centers, that can be viewed as the localization centers of the continuous electronic charge distribution, local electric dipoles develop as the WF centers, with given orbital character, move towards the site with most orbital character of the same kind; in the presence of bond inequivalency, these dipoles are uncompensated, giving rise to a nonzero P . Finally, the polarization can be reversed by reversing OO or the chain dimerization. The unveiled mechanism is different from the one previously reported for undoped manganites[14]. In that case, Jahn-Teller lattice distortions tuned OO, whereas a large Hund coupling in the E-type antiferromagnetic phase constrained electrons to hop along ferromagnetic zig-zag chains; the change of electron motion around each site displaying OO was responsible, through direction-dependent *inter-orbital* hopping processes, for the phase change of the Bloch wavefunctions leading to P .

Even though the analysis has so far been restricted to little more than a toy model, the proposed mechanism may prove relevant for spinel crystals, such as MgTi_2O_4 [27], CuIr_2S_4 [28] or vanadium spinels as ZnV_2O_4 [29] or CdV_2O_4 [22]. In the simplest approximation, the electronic structure of these systems has essentially one-dimensional character, stemming from the strong direct $d-d$ overlap of the B -site t_{2g} orbitals. The strong anisotropy of the d -electron distribution, in fact, is such that electrons in xy, yz, xz orbitals would hop preferably in spinels along xy, yz, xz directions respectively, implying also strongly direction-dependent (orbital-dependent) hopping integrals along each effective one-dimensional “chain”[30]. For instance, in vanadates (V^{3+}) one finds that the xy -orbitals are always occupied due to a tetragonal distortion while the remaining t_{2g} electron moves in degenerate yz, zx bands; adopting Slater-Koster parametrization, the hopping am-

plitudes along a single one-dimensional “chain”, e.g., parallel to yz direction would fulfill $t_{yz, zx} = 0$ and $t_{yz, yz} \simeq 2.8t_{zx, zx}$ [31, 32], close to our choice of parameters. Each chain in the spinel structure may then be subject to Peierls transition, which has been suggested to be strongly tied to possible orbital ordering phenomena[33, 34], eventually driving the system insulator. Interestingly, at least one of the forementioned vanadium spinels, CdV_2O_4 , has been reported to be ferroelectric[22]. Other issues should be taken into account if willing to extend our analysis to more realistic situations, such as the forementioned spinels. In particular, the role of spin degrees of freedom, that has been overlooked in order to highlight the role of orbital degrees of freedom, may play a relevant role in inducing the bond inequivalency, analogously to what happens in $\text{Ca}_3\text{CoMnO}_6$ or in collinear rare-earth manganites RMnO_3 . Furthermore, the interplay between spin and orbital degrees of freedom could be relevant for novel multiferroic or magnetoelectric effects.

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